

CARBON AND SULFUR ISOTOPIC COMPOSITION OF YELLOWKNIFE BAY SEDIMENTS: MEASUREMENTS BY THE SAMPLE ANALYSIS AT MARS (SAM) QUADRUPOLE MASS SPECTROMETER.

H. B. Franz^{1,2}, P. R. Mahaffy¹, J. C. Stern¹, J. L. Eigenbrode¹, A. Steele³, D. W. Ming⁴, A. C. McAdam¹, C. Freissinet¹, D. P. Glavin¹, P. D. Archer, Jr.⁴, A. E. Brunner^{1,5}, J. P. Grotzinger⁶, J. H. Jones⁴, L. A. Leshin⁷, K. Miller⁸, R. V. Morris⁴, R. Navarro-González⁹, P. B. Niles⁴, T. C. Owen¹⁰, R. E. Summons⁸, B. Sutter⁴, C. R. Webster¹¹, and the MSL Science Team. ¹NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, ²University of Maryland Baltimore County, Baltimore, MD 21228, ³Carnegie Institute of Washington, Washington, DC 20015, ⁴NASA Johnson Space Center, Houston, TX 77058, ⁵University of Maryland, College Park, MD 20742, ⁶California Institute of Technology, Pasadena, CA 91125, ⁷Rensselaer Polytechnic Institute, Troy, NY 12180, ⁸Massachusetts Institute of Technology, Cambridge, MA 02139, ⁹Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, ¹⁰University of Hawaii, Honolulu, HI 96822, ¹¹Jet Propulsion Laboratory, Pasadena, CA 91009.

Introduction: Since landing at Gale Crater in August 2012, the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) “Curiosity” rover has analyzed solid samples from the martian regolith in three locations, beginning with a scoop of aeolian deposits from the Rocknest (RN) sand shadow [e.g., 1-3]. Curiosity subsequently traveled to Yellowknife Bay, where SAM analyzed samples from two separate holes drilled into the Sheepbed Mudstone, designated John Klein (JK) and Cumberland (CB). Evolved gas analysis (EGA) of all samples revealed the presence of H₂O as well as O-, C- and S-bearing phases, in most cases at abundances below the detection limit of the CheMin instrument. In the absence of definitive mineralogical identification by CheMin, SAM EGA data can help provide clues to the mineralogy of volatile-bearing phases through examination of temperatures at which gases are evolved from solid samples. In addition, the isotopic composition of these gases may be used to identify possible formation scenarios and relationships between phases. Here we report C and S isotope ratios for CO₂ and SO₂ evolved from the JK and CB mudstone samples as measured with SAM’s quadrupole mass spectrometer (QMS) and draw comparisons to RN.

Experimental Methods: In EGA experiments, powdered solid samples are heated in one of SAM’s pyrolysis ovens to release volatiles. The samples discussed here were processed through a 150 µm sieve before loading. SAM utilizes He carrier gas to sweep volatiles through the gas manifold and QMS, with nominal pressure and flow rate of ~30 mbar and ~1.5 sccm, respectively. The QMS continuously samples the outflow from the pyrolysis oven, scanning over the m/z range of interest. Integration of the QMS signal over time for particular m/z allows quantitative estimates of chemical and isotopic abundance. A portion of the gas stream, parameterized by a desired range of sample temperature, was also collected during each run for isotopic and abundance analysis of CO₂ and H₂O by the SAM tunable laser spectrometer (TLS).

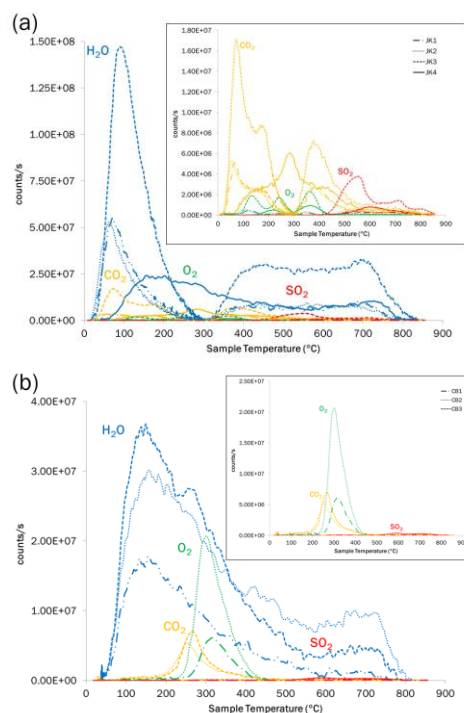


Figure 1. Major volatiles released from drilled samples: (a) JK and (b) CB. Insets show CO₂, O₂, and SO₂ on expanded scale.

During a nominal experiment, the sample is heated to ~850 °C at a rate of 35 °C/min. The RN experiments revealed an instrument background from products of a derivatization reagent, *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA), carried by SAM [4]. In an effort to deconvolve potential contributions to the CO₂ release, various heating protocols were employed at JK and CB. The first three JK runs included a “boiloff” at the beginning of the experiment, in which the sample was held at a temperature of ~200 °C for ~1/2 hour, designed to eliminate instrument background components that would thermally degrade or combust at low temperature before performing the final pyrolysis ramp. Additional measures were taken at CB to reduce adsorption of MTBSTFA to the cup and sample by warming the sample handling system during loading.

EGA Results: All JK and CB samples released H₂O, O₂, CO₂ and SO₂, as shown in Figure 1. This figure shows the major molecular ion for each species for ease of comparing approximate relative abundances. In cases where the major molecular ion saturated the QMS detector, its value was estimated based from other isotopologues for the purpose of this plot. The volatile of greatest abundance in these samples was H₂O, followed by CO₂ and O₂. Abundances of SO₂ released from JK and CB were significantly less than those observed at RN. Further discussion of volatiles released during JK and CB EGA may be found in [5-7].

Carbon isotope ratios: The compound peak shapes of the JK CO₂ EGA traces shown in Figure 1(a) suggest contributions from multiple carbon sources. Candidates for the carbon source are currently being investigated, but include adsorbed CO₂, combusted organic compounds from background or martian sources, and Fe- or Mg-bearing carbonates [8]. Knowledge of the isotopic composition of the various peaks could be helpful in determining relationships between carbon sources.

A selected temperature cut was directed to the TLS for each experiment, allowing high-precision characterization of the carbon isotopic composition of various portions of the gas stream over multiple runs. However, the TLS can only sample a single region in each run, and not all TLS cuts were optimal for CO₂ measurements. Estimating the carbon isotope ratios from QMS EGA data can help fill in the gaps and enhance our understanding of the carbon sources.

Interference from other compounds at m/z 12 and 13 and detector saturation at the major molecular CO₂ ion of m/z 44 typically precluded the use of these m/z values in determining $\delta^{13}\text{C}$ (with respect to V-PDB), which was instead computed from m/z 45 and 46. These calculations require assumptions about the CO₂ oxygen isotopic composition ($\delta^{18}\text{O}$). The CO₂ releases likely represent a mixture of carbon and oxygen from multiple sources. We will consider the effects of various oxygen isotopic compositions on the resulting $\delta^{13}\text{C}$, including $\delta^{18}\text{O}$ values measured by TLS or computed from the EGA O₂ peak, interpreted to represent degradation of an oxychlorine compound [7]. In all cases, $\Delta^{17}\text{O}$ is assumed to be 0.3. Minimum analytical uncertainties in $\delta^{13}\text{C}$ are currently estimated at $\pm 10\%$, based on repeated laboratory EGA analyses [9]. Additional uncertainty arises from background effects and errors in assumption of $\delta^{18}\text{O}$.

We will present the range of $\delta^{13}\text{C}$ obtained for various plausible oxygen sources, bearing distinctive $\delta^{18}\text{O}$ signatures, and discuss implications for the origin of carbon that may have contributed to the CO₂ releases.

For example, ^{13}C -enriched CO₂ has been observed in the atmosphere at Gale Crater with SAM TLS and QMS [10-11]. Given carbonate-CO₂ carbon isotope fractionation factors [12], we will examine the implications of our $\delta^{13}\text{C}$ measurements for formation temperature of carbonates that incorporated atmospheric CO₂.

Sulfur Isotope Ratios: There are a number of Fe- and S-bearing minerals that release sulfur at temperatures consistent with the patterns observed at JK and CB, but the multiple peaks seen in the SO₂ traces suggest that more than one S-bearing phase was present. Based on the temperatures of sulfur release and the EGA traces of relevant m/z values, it is likely that these phases include a sulfide and at least one sulfate mineral [1]. Sulfur released from the sulfide was presumably oxidized in SAM's pyrolysis oven to form SO₂. Possible sources of oxidant for the sulfide include O₂ released from a mineral such as carbonate or perchlorate as well as water-bearing phases.

The sulfur isotopic composition of SO₂ released from Rocknest 1 soil was determined from data at m/z 64, 65, and 66, applying the same assumptions for oxygen isotopic composition as described above for $\delta^{13}\text{C}$ calculations. Uncertainties in $\delta^{34}\text{S}$ (given with respect to V-CDT) are $\pm 10\%$, based on repeated laboratory EGA analyses [6]. Additional uncertainty arises from background effects and errors in assumption of $\delta^{18}\text{O}$.

Our results reveal substantial differences in the $\delta^{34}\text{S}$ values computed for the SO₂ peaks evolved from JK and CB materials. On average, JK samples displayed $\delta^{34}\text{S}$ values close to zero or slightly positive, similar to the composition observed in RN materials and consistent with the range of sulfur isotopic compositions measured in martian meteorites [13-15]. In contrast, CB samples displayed negative $\delta^{34}\text{S}$ values.

The SO₂ EGA peaks are correlated with volatiles released by other phases [16]. In addition, other Curiosity instruments observed distinguishable differences between the JK and CB samples [e.g., 17]. Both observations are pertinent to our interpretation of the sulfur isotopic data. Laboratory analyses designed to identify any potential contributions of instrument effects to the range of observed $\delta^{34}\text{S}$ are ongoing.

References: [1] Blake et al. (2013) *Science* 341. [2] Bish et al. (2013) *Science* 341. [3] Leshin et al. (2013) *Science* 341. [4] Glavin et al. (2013) *JGR* 118. [5] Archer et al. (2014) LPSC XLV. [6] McAdam et al. (2014) LPSC XLV. [7] Sutter et al. (2014) LPSC XLV. [8] Sutter et al. (2013) LPSC XLIV. [9] Franz et al. (2008) LPSC XXXIX, #2433. [10] Webster et al. (2013) *Science* 341. [11] Mahaffy et al. (2013) *Science* 341. [12] Chacko et al. (2008) *GCA* 72. [13] Franz et al. (2010) LPSC XLI, #2341. [14] Franz et al. (2011) LPSC XLII, #2338. [15] Franz et al. (2012) LPSC XLIII, #2232. [16] Eigenbrode et al. (2014) LPSC XLV. [17] Vaniman et al. (2013) *Science*.